

TITLE

ORGANIC FIBERS AND TEXTILE PRODUCTS

Field of the Invention

The present invention relates to an organic fiber having water repellence
5 and oil repellence, to a textile product comprising the fiber, and to a method for
producing the fiber and textile product.

Background of the Invention

It is regarded as desirable for textile products to prevent not only
hydrophilic stains, but also lipophilic stains. Hydrophilic stains can be prevented
10 by means of water repellence, and lipophilic stains can be prevented by means of
oil repellence. Hence, techniques for conferring fibers or textile products with
water and oil repellency have been investigated and, for some applications, have
already been put to practical use. A number of methods are used for conferring
fibers or textile products with stainproofing capabilities arising from such water
15 and oil repelling properties. For example, finishes or coating agents may be used.
That is, the fiber or textile product is immersed in an emulsion or solution of a
silicone polymer, fluorocarbon polymer, polyurethane polymer, vinyl polymer or
a copolymer of any of the above, or a spray containing ingredients such as the
above polymers is applied to the fiber or the textile product, following which
20 drying is carried out so as to form a film on the surface of the fibers. Another
method in current use involves polymerizing monomers or oligomers as
precursors to these polymers on the fiber surface so as to form a film.

However, while covering the entire surface of the textile product with the
above-described film by one of these methods does indeed impart the fibers with
25 stainproofing properties, such an approach has resulted in a considerable loss in
the inherent hand of the fibers. A coating of the above type makes it particularly
difficult to satisfy requirements for breathability and moisture permeability.
While it is also possible to individually coat each fiber or fiber bundle making up
the textile product, when a polymer dispersion is used, a film of smaller thickness

than the size of the particles in the dispersion cannot be formed. In most cases, the film has a thickness of at least several tens of microns, and also lacks adequate strength.

As a result, when the fibers are individually coated with such a coating
5 agent, the coat has a certain thickness, which compromises the hand of the fibers and the textile product. There also exists a thin film-forming method which uses a liquid-type coating, and subjects a polymer precursor on the fiber surface to polymerization and solidification. Unfortunately, it is difficult to obtain a thin film of sufficient durability in this way.

10 Moreover, at the high temperatures which high-strength, high-resistant organic fibers are expected to withstand, the polymers used for coating in this way melt or decompose, and sometimes even ignite. Hence, they lack heat resistance and flame resistance, and are thus ill-suited for applications requiring heat resistance and flame resistance, such as firefighting apparel. Accordingly, there is
15 a desire for fibers, and textile products made thereof, which are endowed with excellent heat resistance and durability with no loss of hand, and which have an excellent stainproofing performance.

Such textile products can be woven products, knit products or nonwoven fabric. Preferred applications include firefighting apparel, gloves and woven
20 fabric for protective clothing.

Summary of the Invention

A composition is provided which comprises an organic fiber comprising a thin film which comprises a fluorocarbon silane.

Also provided is a textile product comprising an organic fiber comprising
25 a thin film which comprises a fluorocarbon silane.

Further provided is a process that can be used for manufacturing a high-strength, heat-resistant fiber or textile product which comprises contacting a fiber or textile product with an aqueous emulsion comprising, or produced by combining, (1) a fluorocarbon silane or its hydrolyzate and (2) optionally a surfactant, an alkoxysilane compound, catalyst, or combinations of two or more
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thereof to produce a fiber or textile-containing mixture and optionally heating the mixture.

Detailed Description of the Invention

Any organic fibers of high-strength, heat-resistance can be used.

- 5 Preferably the fiber can be coated with a thin film comprising a fluorocarbon silane or a thin film comprising a copolycondensate of a fluorocarbon silane with an alkoxy silane. Preferably, a suitable fiber has a strength of about 10 g/D to about 50 g/D, preferably 15 g/D to 50g/D, and a pyrolysis temperature of at least about 300°C, and preferably at least 350°C. Examples of preferred high-strength,
10 heat-resistant organic fibers include wholly aromatic polyamide fibers, wholly aromatic polyester fibers and heterocyclic aromatic fibers, and mixture of two or more fibers.

Suitable wholly aromatic polyamide fibers may be any known aromatic polyamide fibers. Wholly aromatic polyamide fibers are also known as aramid
15 fibers, which are broadly categorized as para-aramid fibers or meta-aramid fibers. Such aramid fibers may be produced and used by any methods known to one skilled in the art. Para-aramid fibers may be any known para-aramid fiber. Illustrative examples of such para-aramid fibers include, but are not limited to, commercial products such as poly(p-phenylene terephthalamide) fibers (produced
20 by E. I. du Pont de Nemours and Company and Du Pont-Toray Co., Ltd. with the trademark KEVLAR®), p-phenylene terephthalamide/p-phenylene 3,4'-diphenylene ether terephthalamide copolymer fibers (produced by Teijin Ltd. under the trade name TECHNORA), or combinations of two or more thereof. Meta-aramid fibers may be any known meta-aramid fibers. Illustrative examples
25 of such meta-aramid fibers include, but are not limited to, commercial products such as poly(m-phenylene terephthalamide) fibers (produced by E. I. du Pont de Nemours and Company under the trademark NOMEX®).

Suitable wholly aromatic polyester fibers may be any known aromatic polyester fibers. Illustrative examples of such wholly aromatic polyester fibers
30 include, but are not limited to, self-condensed polymers of p-hydroxybenzoic acid, polyesters comprising repeat units derived from terephthalic acid and a

glycol, polyesters comprising repeat units derived from terephthalic acid and hydroquinone, polyester fibers comprising repeat units derived from p-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid, or combinations of two or more thereof. Such wholly aromatic polyester fibers may be produced and used by any methods known to one skilled in the art. For example, suitable wholly aromatic polyester fibers include such commercial products made by Kuraray Co., Ltd. under the trade name designation VECTRAN.

Heterocyclic aromatic fibers used in the invention may be any fibers known to one skilled in the art. Illustrative examples of such heterocyclic aromatic fibers include, but are not limited to, poly(p-phenylene benzobisthiazole) fibers, poly(p-phenylene benzobisoxazole) fibers (PBO), polybenzimidazole fibers, or combinations of two or more thereof. Such heterocyclic aromatic fibers may be produced and used by any methods known to one skilled in the art. For example, heterocyclic aromatic fibers include commercial PBO fibers such as those made by Toyobo Co., Ltd. under the trade name designation ZYLON.

The preferred high-strength, heat-resistant organic fibers are aramid fibers made of a para-type homopolymer which are known to one skilled in the art as KEVLAR® or TWARON (made by Teijin Ltd.) for their stability to dimensional change at elevated temperatures such as, for example, peeling of the thin film, for their heat resistance, and for their relatively low cost and good versatility. Preferably, the thin film has a thickness of about 1,000 nm or lower and a strength of 10 to 50 g/D. Also preferred is one or more selected from the group consisting of wholly aromatic polyamide fibers, wholly aromatic polyester fibers, heterocyclic aromatic fibers, and combinations of two or more thereof. p-Phenylene terephthalamide fibers are especially preferred.

The textile products comprise fibers comprising, or coated thereon with a thin film, which comprises or is produced from a fluorocarbon silane or its hydrolyzate, or a copolycondensate of a fluorocarbon silane with an alkoxy silane. Illustrative examples of suitable textile products include, but are not limited to, products obtained by the processing of fibers, such as yarn, batting, woven goods, knit goods, a broad range of nonwoven fabrics, including felt and paper, as well as roving and cord, and combinations of two or more thereof. The textile products

can also include finished goods which are products obtained by these products alone, in combinations thereof, or in combination with other materials, such as resins or metals. The textile products are preferably woven goods, knit goods or nonwoven fabrics. Fire-fighting apparel, gloves and woven fabric for protective clothing are especially preferred.

The high-strength, heat-resistant organic fibers or textile products comprising, or coated thereon with (that is, having a thin film formed on the surface), a thin film of a copolycondensate of a fluorocarbon silane with an alkoxy silane can be produced by treating the organic fibers or the textile products with an aqueous emulsion comprising (1) a fluorocarbon silane hydrolyzate or hydrolyzate thereof, (2) water and optionally (3) a surfactant, an alkoxy silane compound, and a catalyst to produce a fiber- or textile-containing mixture followed by optionally heating the mixture.

The aqueous emulsion can be produced using a fluorocarbon silane and, optionally, a surfactant, a catalyst and an alkoxy silane. It is preferably carried out by dispersing a fluorocarbon silane and an amount of surfactant corresponding to 0.01 to 10, preferably 0.1 to 1 part by weight per part by weight of the overall fluorocarbon silane in water such as to make the fluorocarbon silane content, based on the total weight of the emulsion, from about 0.1 to about 20 wt %, and preferably from 1 to 10 wt %. An acid or alkali catalyst can be added in a catalytic amount (i.e., about 1 to about 1000 ppm final concentration of the emulsion) to the resulting aqueous dispersion, following which an alkoxy silane can be added in an amount corresponding to a mole fraction of 0.1 to 10, and preferably 0.4 to 0.6, based on the fluorocarbon silane to produce a mixture. The mixture of the ingredients can be gently mixed. To obtain a uniform and strong thin film having a thickness of 1,000 nm or less, preferably 500 or less, more preferably 100 nm or less, and even more preferably 50 nm or less, it is preferable to suppress as much as possible the self-condensation reaction by the fluorocarbon silane and/or the alkoxy silane. For this purpose, it is preferable to thoroughly stir the mixture, and to avoid overly rapid addition of the fluorocarbon silane and the alkoxy silane.

The fluorocarbon silane is preferably at least one type of hydrolyzable fluorocarbon silane having the formula $R_f-(CH_2)_p-Si\{-(O-CH_2CH_2)_n-OR^1\}_3$. In the formula, R_f is a C_{3-18} perfluoroalkyl group or a mixture of such groups; the plurality of R^1 groups can be the same or different and are independently one or more C_{1-3} alkyl groups; p is 2 to 4; and n is 2 to 10. R_f is preferably a mixture of perfluoroalkyl groups having an average of 8 to 12 carbon atoms; R^1 represents methyl groups; p is 2; and n is from 2 to 4, preferably 2 to 3. More specifically, when n is 2, a perfluoroalkylethyltris(2-(2-methoxyethoxy)ethoxy)silane is especially preferred. When the letter n is 3, a (2-(2-(2-methoxyethoxy)ethoxy)ethoxy)silane is especially preferred. This type of fluorocarbon silane can be produced by any methods known to one skilled in the art. Two or more fluorocarbon silanes can also be used.

Exemplary alkoxy silanes include organosilicon compounds having at least two alkoxy groups on the molecule, and partial condensation products thereof. Illustrative examples include (1) silicate of the formula $Si(R)_4$ wherein R is one or more group selected from among OCH_3 , OCH_2CH_3 and $(OCH_2CH_2)_mOCH_3$ (m being from 1 to 10); and (2) organoalkoxysilanes of the formula $R^2_nSi(OR^3)_{4-q}$ wherein R^2 is one or more C_{1-10} alkyls; the plurality of R^3 groups are the same or different and independently one or more C_{1-3} alkyls; and q is from 1 to 3). The alkyl group R^2 may be substituted with suitable substituents, such as amino groups, epoxy groups, vinyl groups, methacryloxy groups, thiol groups, urea groups or mercapto groups. Specific examples of suitable alkoxy silanes include, but are not limited to, dimethyldimethoxysilane, methyltrimethoxysilane, 3-aminopropyltriethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldiethoxysilane and 3-glycidoxypropyltrimethoxysilane, and well as mixtures and partial condensation products of any of the above.

Any acid or an alkalilinic substance may be used as the catalyst. Specific examples of suitable acids include, but are not limited to, phosphoric acid, boric acid, hydrochloric acid, sulfuric acid, nitric acid, acetic acid, formic acid, and mixtures of two or more thereof. Specific examples of suitable alkalis include, but are not limited to, ammonia, pyridine, sodium hydroxide, potassium hydroxide, and mixtures of two more thereof. The use of hydrochloric acid or

phosphoric acid as the catalyst in carrying out the invention is especially preferred.

Any surfactants that can stabilize the above-described emulsion may be used. The surfactant generally is a surfactant having an HLB value sufficiently high to inhibit self-condensation of the fluorocarbon silane hydrolysis product. The term "HLB" refers to the HLB system published by ICI America's, Inc., Wilmington, Delaware; Adamson, A.W., "Physical Chemistry of Surfaces", 4th edition, John Wiley & Sons, New York, 1982). The surfactant can be anionic, cationic, nonionic, amphoteric, or combinations thereof. The preferred surfactants are those with HLB values greater than 5, preferably greater than 12, and more preferably greater than 16. Examples of nonionic surfactants include, but are not limited to, $R_f^1\text{-CH}_2\text{CH}_2\text{-O-(CH}_2\text{CH}_2\text{O)}_{11}\text{-H}$, $\text{C}_9\text{H}_{19}\text{-C}_6\text{H}_4\text{-O-(CH}_2\text{CH}_2\text{O)}_{50}\text{-H}$, other nonionic surfactants, and combinations thereof. Examples of cationic surfactants include, but are not limited to $R_f^1\text{-CH}_2\text{CH}_2\text{CH(OH)CH}_2\text{N(CH}_3\text{)}_3^+\text{Cl}^-$, other cationic surfactants, and combinations thereof. Examples of anionic surfactants include, but are not limited to, $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_4\text{OSO}_3\text{NH}_4^+$, $\text{C}_{12}\text{H}_{27}\text{-C}_6\text{H}_4\text{-SO}_3\text{Na}^+$, other anionic surfactants, and combinations of two or more thereof. In each of the formulae, R_f^1 is a perfluoroalkyl group generally having about 3-18 carbon atoms. The preferred surfactants are nonionic surfactants having polyethylene glycol in the molecular chain. The use of a nonionic surfactant, such as $R_f^1\text{-CH}_2\text{CH}_2\text{-O-(CH}_2\text{CH}_2\text{O)}_{11}\text{-H}$ wherein R_f^1 is a C₃₋₁₈ perfluoroalkyl group is preferred.

A variety of additives, including inorganic and organic fillers, antioxidants, heat stabilizers, ultraviolet absorbers, lubricants, waxes, colorants and crystallization promoters, either independently or combinations of a plurality thereof may be used.

The emulsion can be used as is or, if necessary, after dilution or other modification to the desired concentration, by application to the fibers or textile products according to the invention using any means known to one skilled in the art and most suitable to the processing operation carried out in each case such as, for example, impregnation, dipping, coating, or spraying. The emulsion-treated fibers or textile products can be heat-treated at about 150 to about 500, preferably

200 to 450°C, and more preferably at least 250 to 400°C for about 1 minute to about 10 hours, thereby bringing to completion not only hydrolysis of the fluorocarbon silane or hydrolysis of the fluorocarbon silane and hydrolysis of the alkoxy silane, but also copolycondensation of the hydrolyzate. A thin film 5 containing a copolycondensate of a fluorocarbon silane, or its hydrolyzate, and an alkoxy silane can be formed. The heat treatment temperature and time period are preferably set to the optimal values after taking into consideration such factors as the heat resistance of the target fibers or textile product and the cost effectiveness of treatment. The preferred heat treatment temperature or time differs according 10 to the fibers and the textile product. In the case of poly(p-phenylene terephthalamide) fibers, following application of the emulsion, it is especially preferable to carry out heat treatment at about 250°C for about 30 minutes. The ratio of the weight of the copolycondensate coated onto the surface of the high-strength fibers, relative to the weight of the high-strength, heat-resistant organic 15 fibers, is expressed in the dry state following heat treatment and is referred to herein as the "thin film-forming agent picku". This value is generally about 0.1 to 10%. Water generally makes up the rest of the emulsion.

The thickness of the thin film is a calculated value computed from the thin film-forming agent picku and based on the assumption that the fiber cross section, 20 which is generally approximately circular, is a true circle. For example, if the thin film-forming agent picku (based on the fiber weight) is 2% and the fabric weight is 16.7 g, the weight of the coating layer is $16.7 \times 0.02 = 0.334$ g. If the KEVLAR® yarn used in the invention has a density per filament of 1.67 decitex, a length of 100,000 m, and the fibers in the yarn have a circular cross-section and a 25 cross-sectional diameter of 12 µm, the entire surface area is about 3.7680 m^2 ($37,680 \text{ cm}^2$). Assuming that a thin film of the above-described copolycondensate having a specific gravity when dry of about 2 g/cm^3 is uniformly coated over this surface portion, the thin film has a thickness of 44.3 nm.

Before carrying out the above-described emulsion treatment on the fibers 30 or textile product, if necessary or desired, extraneous substances such as finish may be removed from the surface of the fibers by a scouring or solvent scouring operation. Moreover, following the completion of thin film heat treatment, an

operation such as a washing operation to remove residual catalyst and surfactant may be carried out by any means known to one skilled in the art such as water or solvent extraction. Also, the various above-described additives may be suitably added.

- 5 In the practice of the present invention, aside from using high-strength, heat-resistant organic fibers to which has already been applied a thin film of preferably at most 1,000 nm thickness which comprises primarily a fluorocarbon silane or its hydrolyzate, and/or a copolycondensate of a fluorocarbon silane with an alkoxy silane, the invention can also be treated with the above-described
10 10 copolycondensate textile products such as woven fabric composed of the above high-strength heat-resistant organic fibers, protective clothing made of such woven fabric, or protective gloves manufactured directly from the fibers, thereby forming a thin film on the surface of the fibers making up these textile products. Even in cases where formation of the above-described thin film on the fiber
15 15 surfaces or the surface of the textile product involves formation of the thin film on only a portion of the fiber surface or a portion of the textile product surface, such fibers or textiles products shall be regarded as within the scope of the present invention.

Examples

- 20 Examples are given below by way of illustration, although the invention is not limited by these examples.

The fluorocarbon silane used was a mixture of perfluoroalkyl compounds having the formula $R_f(CH_2)_2-Si\{-(O-CH_2CH_2)_2-OCH_3\}_3$ wherein R_f is $F(CF_2)_k$. The compound in which the letter k was 6 accounted for 1 to 2 wt % of the mixture, the compound in which k was 8 accounted for 62 to 64 wt %, the compound in which k was 10 accounted for 23 to 30 wt %, and compounds in which k was 12 to 18 accounted for 2 to 6 wt % of the mixture.

The surfactant was a nonionic surfactant of the formula $R'_f-CH_2CH_2-O-(CH_2CH_2O)_{11}-H$ wherein R'_f was a perfluoroalkyl group of 3 to 18 carbons.

- 30 The organoalkoxysilane was methyltrimethoxysilane $(CH_3)Si(OCH_3)_3$.

Example 1. Preparation of a Fluorocarbon Silane/Alkoxy silane Emulsion.

One hundred parts by weight of a fluorocarbon silane and 30 parts by weight of surfactant were dissolved in water. To the resulting aqueous emulsion was slowly added, under stirring by a conventional stirring technique, 2.5 wt % of the fluorocarbon silane, based on the overall weight of the emulsion, thereby 5 suppressing self-condensation of the fluorocarbon silane and maintaining it in a hydrolyzed state. Next, while measuring the pH of the emulsion with a pH meter, phosphoric acid was added and addition was brought to completion when the pH became 3. Also, methyltrimethoxysilane ($\text{CH}_3\text{Si}(\text{OCH}_3)_3$) was added such as to make the molar fraction of the organoalkoxysilane with respect to the 10 fluorocarbon silane 0.45 and stirring was carried out for 4 hours, yielding a fluorocarbon silane/alkoxysilane emulsion.

Preparation of the Textile Product.

Three strands of 295 dtex (density per filament, 1.67 decitex), 20s/1 two-ply yarn spun from poly(p-phenylene terephthalamide) staple fiber (made by Du 15 Pont-Toray Co., Ltd., Tokyo, under the trademark KEVLAR[®]) were paralleled and fed to an SFG-10 gauge-type glovemaking machine (manufactured by Shima Seiki Mfg., Ltd., Wakayama Prefecture) and knit into 10-gauge gloves. The resulting gloves were ordinarily laundered using a commercial neutral detergent, and dried. Next, the gloves were immersed in the prepared fluorocarbon 20 silane/alkoxysilane emulsion, then lightly wrung by hand so as to adjust the pickup of emulsion non-volatiles to 1%, based on the weight of the glove. Assuming that the fiber cross-section was circular, the film thickness, as 25 computed from the thin film-forming agent pickup, was 22 nm. The gloves were held in a 250°C oven for 30 minutes to effect heat treatment and curing. The gloves were then taken out of the oven and cooled to room temperature, after which they were washed in tepid water and dried. The treated gloves showed no change in hand or appearance compared with prior to treatment. However, when the treated gloves were sprayed with water, the drops of water scattered. The 30 treated gloves demonstrated a striking difference in water repellency compared with untreated gloves.

Example 2. Preparation of Woven Product.

KEVLAR 29[®] yarn (made by Du Pont-Toray Co., Ltd., Tokyo) having a density per filament of 1.67 decitex and composed of 2,000 filaments was used to manufacture plain-weave fabric having a warp density of 17.5 ends/25 mm, a weft density of 16.8 picks/25 mm, and a basis weight of 444 g/m². A 5×5 cm square of the resulting woven fabric was immersed for 5 minutes in the prepared fluorocarbon silane/alkoxysilane emulsion, following which it was drawn out and wrung free of excess fluid so as to adjust the pickup of emulsion non-volatiles, based on the weight of the fabric square, to 1%. This woven fabric was held in a 250°C oven for 30 minutes to effect heat treatment and curing. As in Example 1, the film thus obtained had a thickness of about 22 nm.

Test Example.

(1) Water and Oil Repellency

Drops of pure water and hexadecane were deposited in respective amounts of 2 μl onto the surface of the cured fabric obtained in Example 2, and the contact angle of each fluid was measured with a contact angle meter (manufactured by Kyowa Interface Science Co., Ltd., Saitama Prefecture). The test results are shown in Table 1 below.

In addition, a comparative example was carried out in which drops of pure water and hexadecane were deposited in respective amounts of 2 μl onto the surface of woven fabric produced by the method described in Example 2, but not treated with the fluorocarbon silane/alkoxysilane emulsion. The contact angle of each fluid was measured. The test results are shown in Table 1 below.

Table 1. Water and Oil Repellency

	Example 2	Comparative Example
Water	124°	not measurable due to penetration of water
Hexadecane	109°	not measurable due to penetration of hexadecane

A comparison of the results obtained for woven fabric in Example 2 with the results obtained for the woven fabric in the comparative example showed that water and hexadecane penetrated the untreated fabric, making it impossible to measure the contact angle. By contrast, in Example 2 in which the test was

carried out on a fabric treated with fluorocarbon silane/alkoxysilane emulsion, the fabric exhibited high water and oil repellencies.

(2) Heat Resistance

The treated woven fabric was placed in a 250°C oven and the contact angle was measured after the period of time shown in Table 2 had elapsed. The test results are shown in Table 2.

Table 2. Heat Resistance

	Example 2
Initial water contact angle (degrees)	124
Water contact angle after 3 hours at 250°C (degrees)	127
Water contact angle after 24 hours at 250°C (degrees)	128

The above results showed that, in Example 2, a high water repellency was maintained even after 24 hours at 250°C.

10 (3) Stainproof Properties

One drop of automotive engine oil (engine oil actually used in an automobile for about 1,000 km) was deposited with a pipette in each of three places on a treated woven fabric and an untreated woven fabric, following which the fabrics were allowed to stand for one hour. Laundry detergent (produced by Kao Corporation, Tokyo under the trade name ATTACK) was dissolved in running water to a standard usage concentration of 0.083 wt %. The engine oil-bearing woven fabrics were placed in the synthetic detergent solution and agitated for 5 minutes, then rinsed with running water for 1 minute. Upon comparing the appearances of both types of sample, the oil stain that penetrated the untreated product was found not to have disappeared but the oil stain in the treated product had disappeared completely. Moreover, sufficient water repellency was maintained in the laundered fabric.

The above results show that the present invention provides high-strength, heat-resistant organic fibers endowed with excellent heat resistance and durability and also an excellent stainproofing performance with no loss of hand. By using such fibers according to the invention, there can be obtained textile products such

as firefighting apparel or gloves which, in addition to having excellent cut resistance, flame resistance and dimensional stability at high temperatures, are coated on the fiber surfaces with a water and oil-repelling thin film. Such textile products are resistant to staining and easy to clean. Moreover, because the thin
5 film has a very small thickness, textile products can be obtained in which the characteristics inherent to the constituent fibers, such as their hand, are essentially retained with little or no loss. Furthermore, the invention provides a method capable of manufacturing the above-described fibers and textile products, which method readily imparts a high stainproofing performance due to such water and
10 oil repellency without any loss in the characteristics inherent to high-strength, heat-resistant organic fibers, such as the hand.